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FTD-ID(RS)T-0673-88

FOREIGN TECHNOLOGY DIVISION

ISOMERIZATION OF ISOCYANATES IN THE PRESENCE OF TETRABUTOXYTITANIUM

by

L.F. Tugolukova, E.K. Ignat'yeva, et al.

HUMAN TRANSLATION

FTD-ID(RS)T-0673-88 19 August 1988

MICROFICHE NR: FTD-88-C-000667L

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English pages: 5

Source: Trudy Kazanskoga Khimiko-Tekhnologicheskogo Instituta, Vol. 46, 1971, pp. 66-69

Country of origin: USSR
Translated by: Charles T. Ostertag, Jr.
Requester: AF Astronautics Lab

PREPARED BY:

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WPAFB, OHIO.

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А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ё in Russian, transliterate as yё or ё.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	$\sinh^{-1}$
cos	cos	ch	cosh	arc ch	$\cosh^{-1}$
tg	tan	th	tanh	arc th	$\tanh^{-1}$
ctg	cot	cth	coth	arc cth	$\coth^{-1}$
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian	English
rot	curl
lg	log

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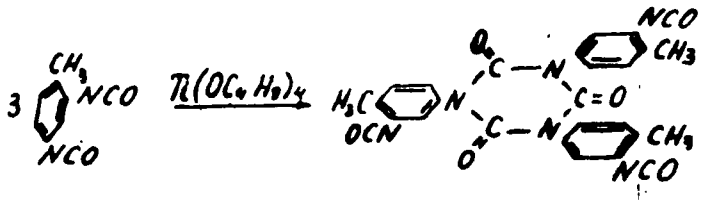
ISOMERIZATION OF ISOCYANATES IN THE PRESENCE OF TETRABUTOXYTITANIUM

**L.F. Tugolukova, E.K. Ignat'yeva,
Ye.V. Kuznetsov, V.N. Petrova**

It is known that hexylisocyanate in the presence of a catalytic amount of tetrabutoxytitanium forms a trimer [1]. It was interesting to investigate the behavior of diisocyanates in the presence of tetraalcoxytitanium.

2,4-toluylene- and 1,6-hyxamethylenediisocyanate were taken as the diisocyanates. The trimer of 2,4-toluylenediisocyanate (2,4-TDI) was obtained in the presence of tetraalcoxytitanium. During prolonged storage it is polymerized, losing its solubility. The formation of the trimer proceeds in the following sequence

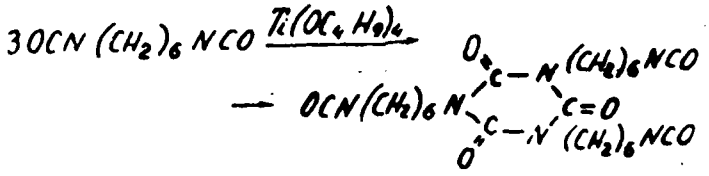


The most reactive isocyanate groups in position 4 participate in the reaction. The ~~following~~ polymerization evidently takes place due

to the remaining isocyanate groups which are found in position 2. The reactivity of this isocyanate group is lowered by a substituent in the ortho-position [2]. In the case of an equimolecular correlation of these components it was not possible to obtain NCO-substituted polyurethane. In this case, just as in the first, the trimer of toluylenediisocyanate is formed with a satisfactory yield.

An increase in the amount of tetrabutoxytitanium leads to a more rapid flowing of the reaction. The trimer is formed instantaneously. The tetrabutoxytitanium which does not enter into the reaction of 2,4-TDI was separated in the form of the condensation product polybutoxytitanium oxane, which is a viscous mass which transforms during reprecipitation into a solid product with a content of up to 83% titanium dioxide. Element analysis, data of IR-spectroscopy and the quantitative content of isocyanate groups confirm the proposed structure of the trimer. In the IR-spectrum of the trimer 2,4-TDI a band of absorption at 1720 cm^{-1} is formed which corresponds to the carbonyl of the isocyanurate ring. This agrees well with data in the literature [3]. The band of absorption at 2216 cm^{-1} corresponds to the isocyanate group.

Hexamethylenediisocyanate (GMDI) is polymerized under analogous conditions. The trimer was not separated, since in aliphatic diisocyanates the reactivity of the isocyanate groups is approximately the same. Their mutual influence is not very noticeable [2]. The polymer is evidently formed through the stage of formation of the trimer:



The free isocyanate groups again enter into the reaction of trimerization, etc. In this case initially a branched, and then a cross-linked polymer of isocyanurate structure is obtained. Some of the isocyanate groups do not enter into the interaction as a result of steric obstacles. Data from IR-spectroscopy testified to the presence in the polymer of a carbonyl group of the isocyanurate ring (1700 cm^{-1}) and an isocyanate group (2216 cm^{-1}). The molecular weight of the polymer, determined based on the content of NCO-groups, was equal to 1800, which corresponds to approximately p=10.

Experimental Section

Trimerization of 2,4-toluylenediisocyanate (2,4-TDI).

a) 5.22 (0.03 moles) of 2,4-TDI and 2 drops of tetrabutoxytitanium were sealed up in an ampoule and held at room temperature for four days. The reaction began immediately after the catalyst was added, which was expressed by a change in the coloring of the reaction mixture, by an increase of its viscosity. On the fourth day the reaction mass was completely crystalized out. Sometimes a transparent block was formed. The trimer was purified by reprecipitation from chloroform by diethyl ether.

Found, %: C - 63.33; 63.92. No. 15.06; 14.52.

Calculated, %: C - 62.07; No. 16.09.

b) 10.2 g (0.03 moles) of tetrabutoxytitanium was placed in a three-neck flask equipped with a mixer, a dropping funnel and a thermometer. 5.22 g (0.03 moles) of 2,4-TDI in a current of nitrogen were added dropwise to it slowly while mixing. Immediately a crystalline product began to form - the trimer 2,4-TDI. The reaction proceeds with the liberation of heat. The temperature of the reaction mixture was raised by 18°C. Further the reaction mixture was held for 24 h at room temperature, after which it was processed with several batches of diethyl ether. A large share of the mixture was dissolved. 4.6 g (86%) of trimer 2,4 TDI remained in the precipitate.

Found, %: C - 62.10; 62.20. No. 17.29; 17.44.

Calculated, %: C - 62.07; No. 16.09.

A viscous mass was separated from the ether and after reprecipitation it hardened.

The yield of solid product was 2 g, which is 72%.

Found, %: C - 9.61; 9.04. H - 3.15; 3.29; TiO_2 83.62; 83.10.

Calculated, %: C - 9.60; H - 1.3; TiO_2 - 88.9.

Polymerization of hexamethylenediisocyanate. 4.54 g (0.027 moles) of GMDI and 2 drops of tetrabutoxytitanium were sealed in an ampoule and held at room temperature for 10 days. A transparent block of the polymer hexamethylenediisocyanate was formed. The polymer was ground into powder and washed with several batches of ether.

Found, %: N 16.82; 16.44.

Calculated, %. N 16.66.

Conclusions

1. Tetrabutoxytitanium catalyzes the reaction of trimerization of toluyleneisocyanate independent of their correlation.

2. Hexamethylenediisocyanate in the presence of tetrabutoxytitanium forms a polymer.

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